

QUANTUM SOLIDS

New Phases for the Ordering of Quantum Rotors in 2D: NMR Studies

Sullivan, N.S., UF, Physics/NHMFL
Kim, K., Stanford Univ., Physics

NMR experiments at moderately high magnetic fields (~ 7 T) have been carried out to study the orientational ordering of ortho-para hydrogen molecules physisorbed on hexagonal boron nitride. The studies were carried out for layer coverages corresponding to the density expected for the commensurate $\sqrt{3} \times \sqrt{3}$ structure with one molecule occupying the center of every third hexagon of the hexagonal lattice of the

boron nitride. The system consists of a 2D ensemble of interacting quantum quadrupoles (ortho-hydrogen molecules) with angular momentum $J=1$. The commensurate coverage is especially interesting because of the high geometrical frustration imposed on the ordering of the hydrogen molecules by the triangular lattice for the fixed centers of mass of the molecules.

Distinctly different NMR line shapes are observed for different concentrations and this has been used to identify four different orientationally ordered phases illustrated schematically in Figure 1:

- (1) A high concentration long range ordered pinwheel phase (PW) in which the molecular alignments $S_i = \langle 3J_{zi}^2 - J^2 \rangle$ are all -2 at each site

with the local axes z_i aligned in a pinwheel configuration

- (2) A 2D quadrupolar glass state at intermediate temperatures and intermediate concentrations for which the molecular alignments S and local axes are distributed at random
- (3) A herringbone phase (HB) that evolves continuously to a purely local crystal field ordering at low concentrations
- (4) An unusual and unexpected hindered rotor state (HR) at very low temperatures for which the orbital magnetization $\langle J_z \rangle$ is non-zero.

The long-range pinwheel phase is fragile with respect to dilution with non-interacting para-hydrogen molecules ($J=0$) and there is an abrupt (apparently first order) transition at a critical concentration of 69% to the glass state. The quadrupolar glass state is a tensorial "spin-1" glass and is believed to result from the combined effects of frustration and substitutional disorder.

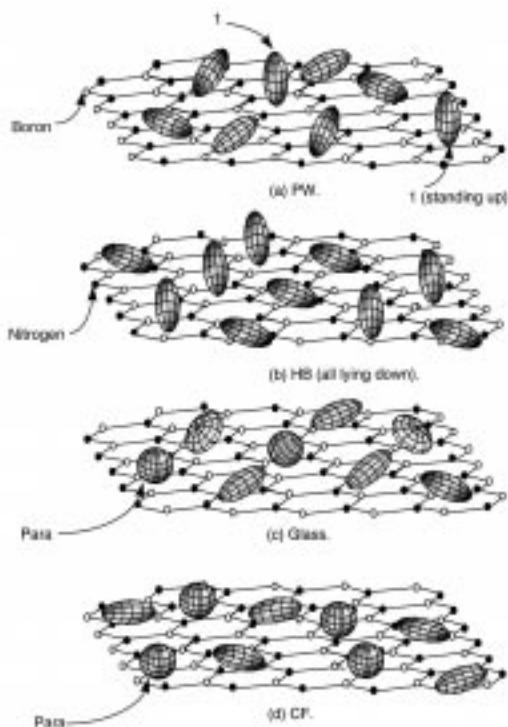


Figure 1. Schematic representation of the different orientational ordered phases for hydrogen molecules in a $\sqrt{3} \times \sqrt{3}$ commensurate triangular lattice on a substrate of BN: (a) pinwheel phase (PW), (b) herringbone structure (HB), (c) quadrupolar glass state, and (d) a locally ordered crystal field state (CF).

Theory of the Ordering of Molecular Hydrogen in 2D

Sullivan, N.S., UF, Physics/NHMFL

Kim, K., Stanford Univ., Physics

The orientational ordering of ortho-hydrogen molecules in two dimensions is of considerable interest as the quantum correlations and geometrical nature of the frustration of the interactions play a dominant role in determining the nature of the ordering. Moderately high field NMR studies¹ have recently shown that the transitions to the periodic pinwheel ordered geometry in 2D are first order. A complex phase diagram (Figure 1) is observed as a function of the concentration of ortho-hydrogen (orbital momentum $J = 1$). Long range order is only observed above a critical ortho concentration of 69%. This critical concentration is much higher than the value of 55% observed for 3D samples.

The method of restricted traces² has been used to calculate the free energy functional for the ordered states as a function of the long-range order parameter, $S = \langle 3J_z^2 - J^2 \rangle$, which is the molecular alignment along one of the local symmetry axes Z . The free energy can be expanded in terms of cumulants and the minima of the free energy determined as a function of S for a given temperature. For high temperatures there is only one minimum for $S=0$, but at low temperatures a second minimum occurs at finite S . A first order phase transition therefore occurs at the temperature for which the two minima have equal depth.

The first cumulant is the mean energy, $M_1 = 6NX^2 S^2(1-1/N)$, where N is the number of molecules, X the ortho concentration and Γ gives the strength of the quadrupole-quadrupole interaction, V_{ij}^Q , that drives the ordering. The second order cumulant,

$$M_2 = 6NX^2\Gamma^2(2-S-S^2)[(2-s-\alpha S^2)],$$

gives the quantum fluctuations in the order parameter for the ordered configuration. α is a geometrical factor determined by the sublattice structure and is simply

given by the ratio of sum of three-particle ($V_{ij}V_{jk}$) and four particle diagrams ($V_{ij}V_{kl}$) to the pair wise terms ($V_{ij}V_{ji}$) that occur in M_2 . $\alpha = 2X-1$ for the Pa3 order in 3D, and $\alpha = (3X-2)/2$ for the pinwheel order on a triangular lattice. The critical concentrations are therefore close to 50% and 67% for 3D and 2D, respectively.

Detailed calculations of the free energy have been carried out and the transition temperatures, $T_c = k_B/\beta_c$, predicted as a function of ortho concentration, are given by

$$\beta_c = 3(X-V_c) - \sqrt{[9(X-V_c)^2 - 2X\xi \log 2]}/6X\xi,$$

where $\xi = 2.2 + 0.2\alpha$ and V_c measures the ratio of the surface crystal field to Γ . The dashed line in Figure 1 shows the calculated transition temperatures which are in good qualitative agreement with the observed values.

References:

- 1 Sullivan, N.S., *et al.*, J. Low Temp. Phys., **111**, 533-543 (1998).
- 2 Kirkwood, J.G., J. Chem. Phys., **6**, 70 (1938).

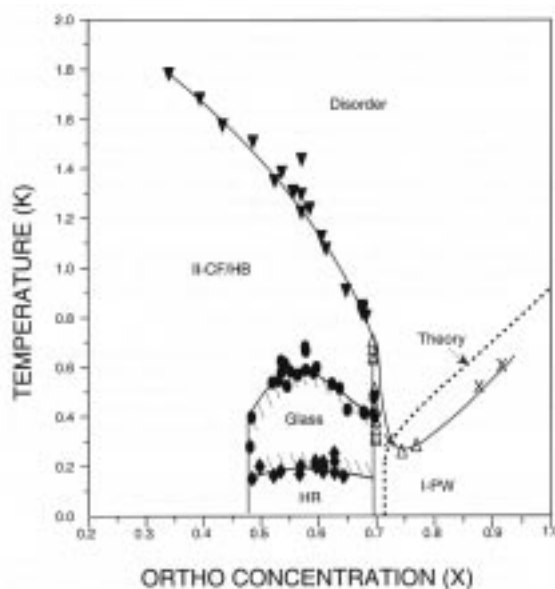


Figure 1. Phase diagram for the orientational ordering of molecular hydrogen in two dimensions. PW refers to the pinwheel phase, CF the local ordering due to crystal fields, and HR is the hindered rotor state. The symbols designate transitions inferred from changes in NMR line shapes. The solid line corresponds to the experimentally determined phase boundaries and the dashed line is the result of the calculation reported above.